

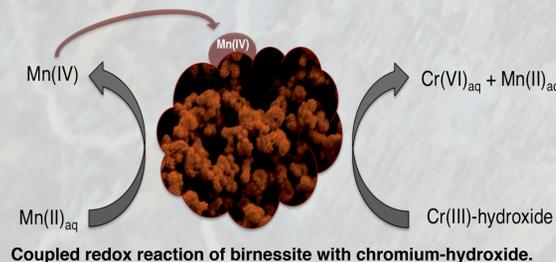
Oxidation of mixed Cr-Fe hydroxides by birnessite

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Introduction

Chromium is found natively in serpentinites and ultramafic rocks which comprise $\approx 1\%$ of the land surface (Oze, 2007), most notably around convergent plate boundaries such as the Pacific Rim and Mediterranean. Weathering and diagenetic processes enrich Cr(III) in sediments, and release Cr(III) that often precipitates with Al/Fe(III)-hydroxides. Coupled biotic and abiotic processes can result in the formation of secondary Cr(III)-minerals (e.g., mixed Cr-Fe hydroxides) that range in solubility. In fact, Berger and Frei (2014) found that enrichment of Fe and Al in soils is a characteristic feature of laterite and can be correlated with Mn and Cr. Here, we used mixed Cr(III)/Fe(III)-hydroxide precipitates, which have solubilities decreasing with increasing Fe substitution, to investigate the rate of Cr(VI) generation through reaction with Mn-oxides (the principal oxidant of chromium). The information provided in this study will be useful to help predict the potential and rate-controlling factor in chromium oxidation of both native chromium-bearing phases and those produced through in situ subsurface remediation.



Methods

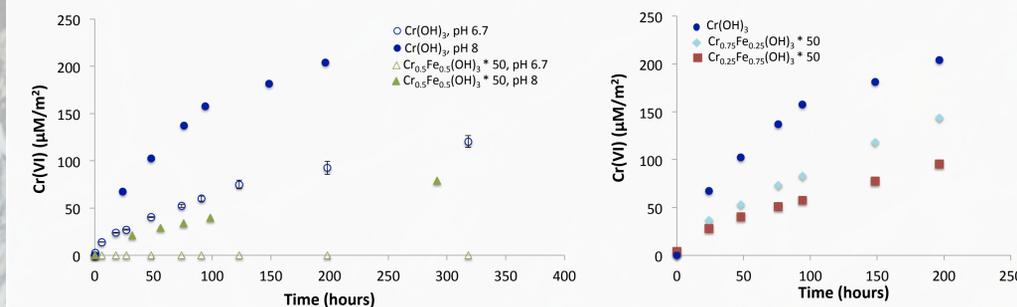
SYNTHESIS: Birnessite was synthesized using the procedure described in Buser *et al.* (1954) and modified by Ying *et al.* (2011). Chromium-hydroxide was synthesized by titrating 20 mM CrCl₃ to pH 6 and maintained for 24 h (Fendorf *et al.*, 1994). A series of Fe_{1-x}Cr_x(OH)₃ were synthesized by titrating stoichiometric concentrations of FeCl₃ and CrCl₃ solutions with 0.1M NaOH to pH 7; pH was maintained for 3 days. Ratios of Fe(III):Cr(III) were verified with X-ray fluorescence spectrometry (XRF).

BATCH REACTORS: Batch reactors were run using mixed Cr-Fe hydroxides (Fe_{1-x}Cr_x(OH)₃, with x ranging from 1 to 0.25). A 10 mM acetate buffer was used for vials at pH 5, 10 mM PIPES at pH 6.7, and 10 mM HEPES at pH 8.

ANALYSIS: Spectrophotometric methods were used to measure soluble Cr(VI) as outlined in Bartlett and James (1979). Total dissolved Cr, Fe, and Mn were measured by inductively coupled plasma mass spectrometry (ICP-MS). SEM, TEM, BET, and XRD were used for solid phase characterization.

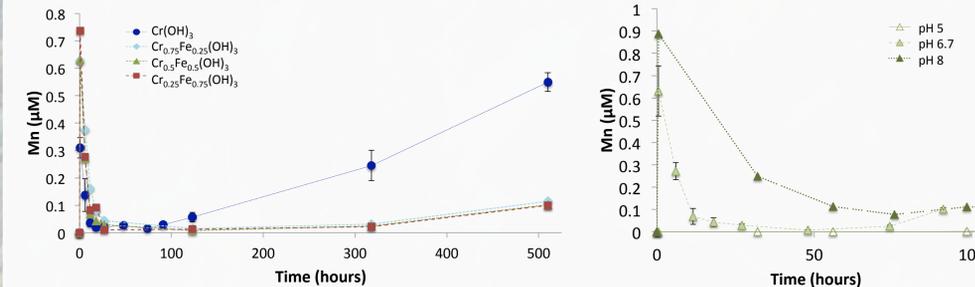
Results

Chromium(VI):



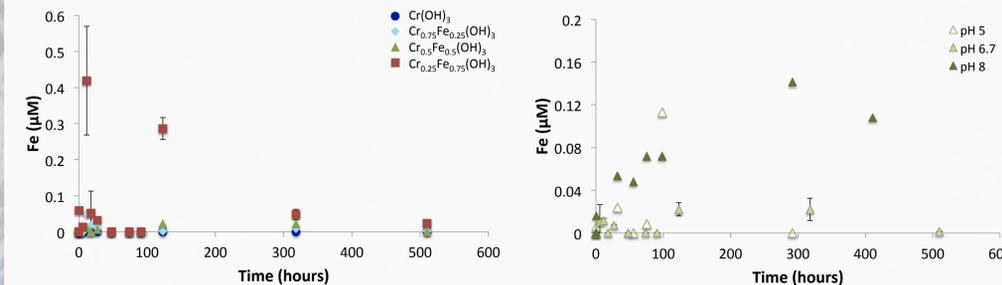
Cr(VI) generated as a function of time and pH upon reaction of Cr(OH)₃ and Fe_{0.5}Cr_{0.5}(OH)₃ with birnessite (left). Error bars represent standard deviation of treatments performed in triplicate. Cr(VI) produced from a series of Fe-substituted Cr(OH)₃ reacted with birnessite at pH 8 (right). Concentrations normalized by Cr/Fe-hydroxide surface area. Standard error less than 10% for all treatments.

Manganese:



Aqueous production of Mn²⁺ generated from birnessite reacting with Fe-substituted Cr(OH)₃ at pH 8 (left). Error bars represent standard deviation of triplicates. Mn²⁺ produced as a function of pH upon birnessite reaction with Cr_{0.5}Fe_{0.5}(OH)₃ (right).

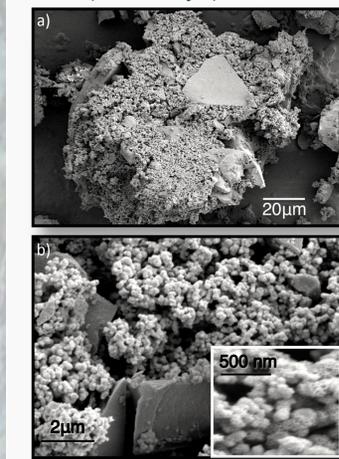
Iron:



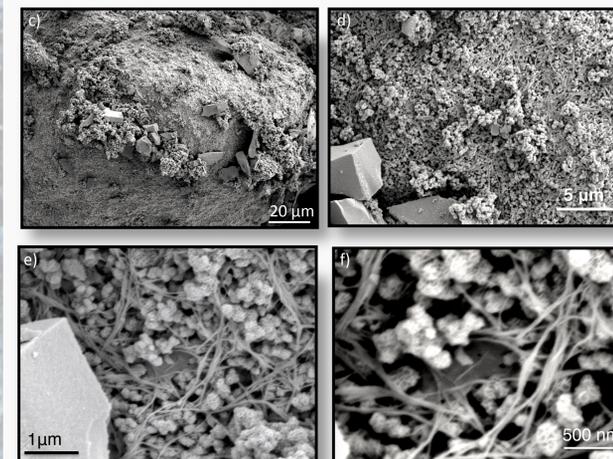
Aqueous Fe²⁺ production as a function of iron-substitution upon reaction of Cr/Fe(OH)₃ with birnessite at pH 8 (left). Error bars represent standard deviation of triplicates. Fe²⁺ produced as a function of pH upon birnessite reaction with Cr_{0.5}Fe_{0.5}(OH)₃ (right).

Imaging

Initial (t = 0 days)



Endpoint (t = 35 days)

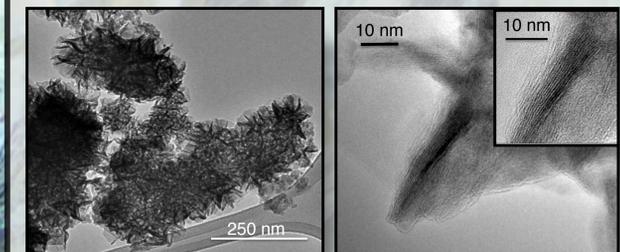


SEM images of initial (a-b) and final (c-f) Cr_{0.5}Fe_{0.5}(OH)₃ and birnessite mixtures. Formation of α -MnO₂ resembling todorokite becomes visible as the reaction progresses.

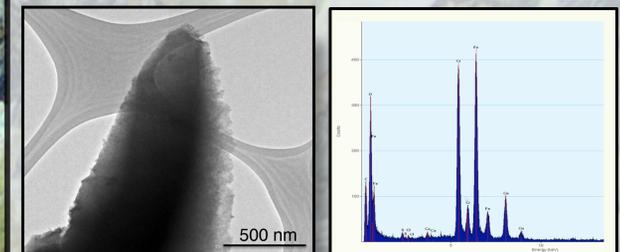
Conclusions

- Cr(VI) is produced at all pHs and with all solids (reacted with birnessite) investigated.
- The rate and extent of Cr(VI) production scaled with the solubility of the Cr/Fe(OH)₃ solids. Pure Cr-hydroxide yielded the highest Cr(VI) production and Cr_{0.25}Fe_{0.75}(OH)₃ the least.
- Aqueous Cr(VI) was greatest at pH 8 due, in part, to diminished HCrO₄⁻ adsorption.
- Over the course of the reaction, a network of α -MnO₂, with a thread-like morphology consistent with the tunnel structure of todorokite, are produced and mix with birnessite needle clusters.

TEM Characterization



TEM images of synthesized birnessite.



TEM image of Cr_{0.5}Fe_{0.5}(OH)₃ and confirmation by EDS analysis. Sample taken 35 days into reaction with birnessite at pH 6.7.

Acknowledgements

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References

- Bartlett R; James B (1979) Behavior of chromium in soils: III. Oxidation. *J. Environ. Qual.* 8, 31-35.
- Berger A; Frei R (2014) The fate of chromium during tropical weathering: A laterite profile from Central Madagascar. *Geoderma* 213: 521-532.
- Buser W; Graf P; Feitknecht W (1954) Beitrag zur kenntnis der mangan (II)-manganit und des δ -MnO₂. *Helv. Chim. Acta* 37: 2322-2333.
- Fendorf SE; Lamble GM; Stapleton MG; Kelley MJ; Sparks DL (1994) Mechanisms of chromium(III) sorption on silica. 1. Cr(III) surface structure derived by extended X-ray absorption fine structure spectroscopy *Environ. Sci. Technol.* 28: 284-289.
- Hansel CM; Weilinga BW; Fendorf S (2003) Structural and compositional evolution of Cr/Fe solids after indirect chromate reduction by dissimilatory iron-reducing bacteria. *Geochim. Cosmochim. Acta* 67: 401-412.
- Oze C; Bird DK; Fendorf S (2007) Genesis of hexavalent chromium from natural sources in soil and groundwater. *Proc. Natl. Acad. Sci.* 104: 6544-6549.
- Ying SC; Kocar BD; Griffis SD; Fendorf S (2011) Competitive microbially and Mn oxide mediated redox processes controlling arsenic speciation and partitioning. *Environ Sci Technol.* 45: 5572-5579.